20.4 Electric Field Mass Analyzers

- time-of-flight analyzers are based on different masses having different velocities
- quadrupole mass filters are based on stable ion trajectories in oscillating quadratic electric fields
- quadrupole mass filters can be scanned with unit resolution at 1,000 Th s\(^{-1}\)
- ion traps are three-dimensional quadrupoles that can be adapted to Fourier transform detection
- both linear quadrupoles and traps are useful in MS/MS experiments
Time-of-Flight (TOF) Analyzers

The basic scheme is shown in the figure, where MALDI is used to produce the ions. The ions are accelerated towards the grounded aperture by 20 kV. This gives each ion about the same kinetic energy.

\[
\frac{mv^2}{2} = qV_s = zeV_s
\]

The time required for each ion to travel a distance, \(d\), through the field-free region depends upon the mass to charge ratio.

\[
t^2 = \frac{d^2}{v^2} = \frac{m}{z} \left( \frac{d^2}{2V_se} \right)
\]

The lower the mass of the ion, the faster it will arrive at the detector. In principle there is no upper mass limit. In practice, ions as heavy as 300 kTh have been observed with MALDI ionization.
Linear TOF analyzers have poor resolution, 150-200, due to:
• spread in time required to produce the ions
• size of the volume within which the ions are produced
• spread in kinetic energy when the ions are formed

The reflectron TOF has a series of concentric rings that produce a
retarding field that acts like an ion mirror. For two ions with the
same mass and different kinetic energy, the fastest traveling will
travel farther into the "mirror," making it follow a longer path to the
detector.

Commercial units have a resolution of 6,000 with an upper mass
range of 1-50,000 amu in 1 ms.

The ion labeled □ has a
lower kinetic energy
(lower velocity) than the
ion labeled ■ (higher
velocity).
An ideal quadrupole has rods with a hyperbolic shape. In practice four cylindrical rods are used - length ~10 cm, diameter ~ 1 cm, and r0 ~0.3 cm. The short length means that pressures ×10 above magnetic analyzers can be used. This is convenient for MS/MS.

Ions are accelerated by ~10 V into the region between the four rods. The rods have both a dc and ac voltage applied to them.

\[ \Phi_+ = [U - V \cos(2\pi ft)] \quad \Phi_- = -[U - V \cos(2\pi ft)] \]

The value of f is ~1 MHz. Typical values for U are 0-250 V and for V are 0 - 1,500 V. When scanning the filter U and V are varied with the ratio of V/U kept constant at ~6.
The transverse spatial distribution of the electric potential is given by the following expression,

\[ \Phi_{x,y} = \frac{x^2 - y^2}{r_0^2} \left[ U - V \cos(2\pi ft) \right] \]

where \( x \) and \( y \) are distances from the center centerline and \( 2r_0 \) is the axial rod spacing. The equation is \( x,y \)-factorable.
The electric field applies a force to the ion. The force can be used to compute the distance moved within one cycle, $t$, of the radiofrequency field.

\[ F = ma = -zq \frac{\partial \Phi}{\partial x} \]

\[ m \frac{x}{t^2} = -zq \frac{\partial \Phi}{\partial x} \]

\[ x = -\frac{zqt^2}{m} \frac{\partial \Phi}{\partial x} \]

Heavier masses move smaller radial distances. This makes the rf-only quadrupole a high-pass mass filter. The low masses pick up sufficient kinetic energy to hit the rods and get neutralized.
Heavy masses do not respond to the ac field. The dc field pushes them toward the center and passes them.

Light masses respond to both the ac and dc fields. The ac field pulls ions toward the rods. Then both fields push the ions toward the center, accelerating them to higher than their initial velocity. They continue picking up energy until they hit the rods.
Heavy masses do not respond to the ac field. The dc field pulls them outward until they hit the rods.

Light masses respond to both the ac and dc fields. Both the dc and ac field pull ions toward the rods. Then the ac field pushes the ions toward the center. The acceleration going through zero is not as great as the highpass filter so they don't reach the rods.
Equations of Motion

The electrical potential can be factored into x and y components.

\[
\Phi_x = \frac{x^2}{r_0^2} \left[ U - V \cos(2\pi ft) \right] \quad \Phi_y = -\frac{y^2}{r_0^2} \left[ U - V \cos(2\pi ft) \right]
\]

The electrical potential can then be used to compute the force on the ion along each axis.

\[
F_x = m \frac{d^2 x}{dt^2} = -zq \frac{\partial \Phi}{\partial x} \quad \quad F_y = m \frac{d^2 y}{dt^2} = -zq \frac{\partial \Phi}{\partial y}
\]

The result is two separate equations of motion for the ion.

\[
\frac{d^2 x}{dt^2} + \frac{2zq}{mr_0^2} \left[ U - V \cos(2\pi ft) \right] x = 0
\]

\[
\frac{d^2 y}{dt^2} - \frac{2zq}{mr_0^2} \left[ U - V \cos(2\pi ft) \right] y = 0
\]
The Mathieu Equation

By defining the following variables, the equations of motion can be put into a form solved by the physicist Mathieu in 1866.

\[
\xi = \frac{2\pi ft}{2} \quad a_u = a_x = -a_y = \frac{8zqU}{m(2\pi f)^2 r_0^2} \quad q_u = q_x = -q_y = \frac{4zqV}{m(2\pi f)^2 r_0^2}
\]

\[
\frac{d^2u}{d\xi^2} + (a_u - 2q_u \cos(2\xi))u = 0
\]

The Mathieu equation needs to be solved numerically. The figure shows the four regions in the \(a,q\)-plane where the equation has stable solutions. The inset shows a detail for the region with the smallest values of \(a\) and \(q\).

A unstable solution means that the oscillating amplitude is increasing without bounds - thus will hit the rods.
A mass stability diagram is simply the solution stability diagram with \( a \) and \( q \) converted back into \( U \) and \( V \). Each ion has its own stable area on the diagram. The figure shows three ions with \( m_1 < m_2 < m_3 \).

A highpass mass filter has \( U = 0 \) and \( V \) fixed. For example, \( V = V' \) passes \( m_2 \) and \( m_3 \) but not \( m_1 \).

By increasing \( V \) while keeping \( U/V \) constant, a straight line is scanned. The slope of the line determines the resolution. Line \( S \) passes close to the apex of the stability diagrams and has unit resolution. Line \( S' \) cuts across several stability diagrams and has less than unit resolution.

Voltage can be scanned as fast as 1,000 Th \( s^{-1} \). This makes scanned quadrupole filters compatible with GC detection.
The ion trap is a quadrupole that is bent on itself to form a closed loop. It is in essence a three-dimensional quadrupole where all stable ions are trapped within the device.

The potential $+\Phi$ is applied to the ring electrode with $-\Phi$ applied to the cap electrodes. The equations of motion can be reduced to a Mathieu form to obtain stability diagrams.

To obtain a spectrum, the voltage is scanned. As each m/z becomes unstable the ions are ejected through a hole in the end cap.
The example below shows an electrospray source with the resultant ions injected into the trap through a hole in the end cap. Detection of specific m/z ions is achieved by ejection through a hole in the opposite end cap.

Ion traps are of great interest because they can be miniaturized. Also, like all electric field techniques they do not need a magnet. Finally, ion traps can be operated in a Fourier transform mode to decrease the amount of time required to obtain a spectrum.